

# **Application of Ion-Exchange Technology for Perchlorate Removal from San Gabriel Basin Groundwater**

**Final Project Report**

Submitted to:

**Main San Gabriel Basin Watermaster**

**725 North Azusa Avenue**

**Azusa, CA 91702**

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## Acknowledgement

*This product is the result of the dedication and hard work of many individuals. Specifically, the following individuals are acknowledged for their support and contribution to the project:*

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Bob Bowcock	-	Board Member

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# Executive Summary



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## Executive Summary

- ◆ This study focused on evaluating the removal of perchlorate from groundwater using ion-exchange technology.
- ◆ Both bench- and pilot-scale testing was conducted using groundwater from the San Gabriel Basin containing perchlorate (200 ug/L during bench-scale testing & 90 ug/L during pilot-scale testing).
- ◆ Polyacrylic and polystyrene resins were evaluated for their ability to remove perchlorate, as well as their ability to release perchlorate upon regeneration.
- ◆ Polystyrene resins have extremely high capacities for perchlorate, but are very difficult to regenerate.
- ◆ Polyacrylic resins seem to have the right balance between moderate capacity and ease of regeneration.
- ◆ Two polystyrene resins (ASB2 and IRA400) and two polyacrylic resins (IRA458 & A850) were evaluated.
- ◆ The results show that, for the A850 resin, approximately 725 bed volumes were achieved before perchlorate breakthrough occurred. Breakthrough is defined as the time at which the concentration of perchlorate in the effluent reaches its detection limit of 4 ug/L. The influent concentration of perchlorate in these tests was approximately 90 ug/L.
- ◆ When the run was terminated at the breakthrough criteria described above, a salt loading rate of 30 lbs/ft<sup>3</sup> was consistently sufficient to fully regenerate the A850 resin.
- ◆ Biological reduction of nitrate and perchlorate from the brine was also investigated. During the short course of the study, nitrate removal was easily achieved. However, additional acclimation time was necessary for perchlorate reduction to occur.
- ◆ Using an example analysis, the capital cost of a 2500 gpm ion-exchange system for perchlorate removal from the San Gabriel Basin was estimated at \$1,735,000, with an annual O&M cost of \$305,000/yr. The total annual cost was estimated at \$445,000/yr, which translates into a water cost of approximately \$122/AF. It should be emphasized that these costs are only estimates and should not be used for bidding purposes.

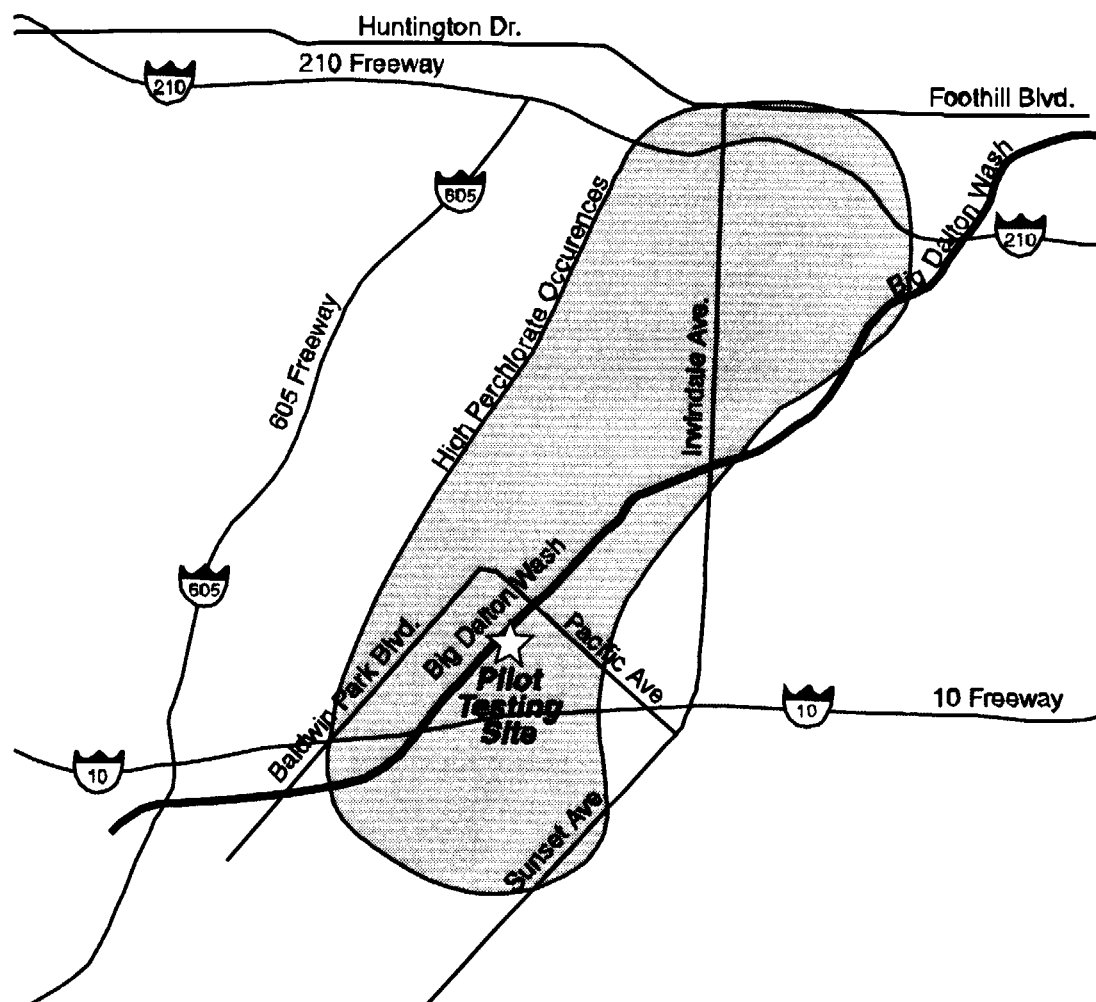


# Background



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## Occurrence of Perchlorate in the San Gabriel Basin



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## Perchlorate Uses, Health Effects, & Regulatory Requirements

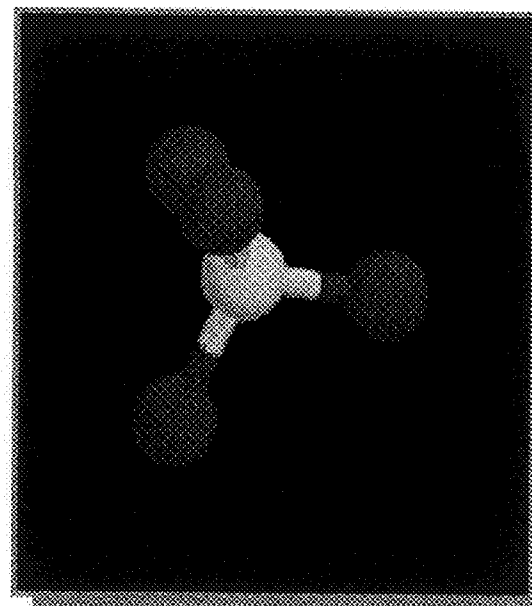
- ◆ Perchlorate ( $\text{ClO}_4^-$ ) contamination in the environment originates from its salts of ammonium perchlorate ( $\text{NH}_4\text{ClO}_4$ ), potassium perchlorate ( $\text{KClO}_4$ ), or sodium perchlorate ( $\text{NaClO}_4$ ).
- ◆ Since the 1950's, perchlorate has been used as an oxygen-adding component in solid rocket fuel, and has been used on missiles, rockets, and the space shuttle, as well as fireworks.
- ◆ As such, primary users of perchlorate have included the US Department of Defense and its contractors, NASA, and other entities that has responsibilities for manufacturing, handling, storing, testing, or using solid rocket fuel.
- ◆ As a result of handling perchlorate in several facilities in California, Nevada, Texas, and Utah, (and likely other states) release of residual perchlorate into the environment resulted in the contamination of various groundwaters with the perchlorate ion.
- ◆ The health effects of perchlorate are linked to its impact on the thyroid gland function which results in suppressed production of growth hormones by the thyroid gland.
- ◆ In 1997, the California Department of Health Services (DHS) adopted a provisional perchlorate action level of 18 ug/L.
- ◆ In December, 1998, the USEPA issued a draft report that estimated the perchlorate Reference Dose (RfD) at 0.0009 mg/kg/day. However, the report cautioned that this RfD may be reduced to 0.0003 mg/kg/day pending agency review.
- ◆ Assuming typical USEPA approach for calculating drinking water levels (70 kg person drinking 2 liters of water per day), the RfD of 0.0009 mg/kg/day translates into a maximum drinking water level of 32 ug/L. However, a RfD of 0.0003 mg/kg/day translates into a maximum drinking water level of 11 ug/L.
- ◆ As of February 1999, the minimum reporting limit for perchlorate analysis is 4 ug/L.





## Perchlorate Analysis in Water

- ◆ Perchlorate samples were analyzed by Montgomery Watson Laboratories
- ◆ Modified EPA method 300 was used.
- ◆ A Dionex Ion-Chromatograph (IC) equipped with an ionpac AS11 analytical column, a Dionex ionpac AG11 guard column, and a Dionex CD20 detector were used.
- ◆ Perchlorate concentration in high TDS brine solution was determined by pretreating the sample with a strong acid cationic exchange resin loaded with silver ( $\text{Ag}^+$ ). When the sample is exposed to the cationic resin, the sodium exchanges with the silver on the surface of the resin, and the silver reacts with the chloride to precipitate as  $\text{AgCl}$ . The resulting solution, with reduced sodium and chloride, is then analyzed in the same manner discussed above.



## Fundamentals of Ion-Exchange Technology for Perchlorate Removal



- ◆ The above reaction is the primary ion-exchange reaction that occurs on the surface of a strong-base anionic exchange resin in the chloride form used for perchlorate removal.
- ◆ The chloride ion ( $Cl^-$ ) on the surface of the quaternary amine group ( $R_4N^+$ ) is exchanged for the perchlorate ion ( $ClO_4^-$ ) present in the water.
- ◆ However, many other anions commonly present in the water will compete with the perchlorate ion for this reaction. These include sulfate ( $SO_4^{2-}$ ), nitrate ( $NO_3^-$ ), bicarbonate ( $HCO_3^-$ ), carbonate ( $CO_3^{2-}$ ), and bromide ( $Br^-$ ).
- ◆ Other trace ions can also compete with the perchlorate ion for the resin surface. These include arsenic ( $HAsO_4^{2-}$ ) or selenium ( $SeO_3^{2-}$ ), chlorate ( $ClO_3^-$ ), and bromate ( $BrO_3^-$ ).
- ◆ Once the resin is loaded with the perchlorate ion, it is regenerated with a salt solution ( $NaCl$ ). However, in order for the chloride to substitute the perchlorate ion, it has to be present at very high concentrations in the brine solution. Therefore, the brine solution can range from 3% salt (about 31,000 mg/L of  $NaCl$ ) to as high as 20% salt (about 250,000 mg/L as  $NaCl$ ).
- ◆ Once the resin is re-loaded with chloride, it is put back in service, and the ion-exchange cycle is repeated.



## IX Resins for Perchlorate Removal

- ◆ Two types of resins were evaluated in this study: hydrophobic resins (polystyrene resins) & hydrophilic resins (polyacrylic resins). These resins have vastly different affinities for perchlorate.
- ◆ Affinity of an IX resin for an ion is quantified by the factor,  $\alpha_{Cl^-}^X$ , which is a measure of the relative affinity of the resin to an anion,  $X^-$ , compared to its affinity for the chloride ion. Therefore, a higher a value indicates a higher affinity of the resin for the anion.
- ◆ Based on the values listed below, polystyrene resins have a very high affinity for perchlorate, whereas polyacrylic resins have a moderate affinity for perchlorate. This suggests that service time of a polystyrene resin is much higher.
- ◆ However, higher affinity also means that the resin is difficult to regenerate, which increases its operating cost.
- ◆ Therefore, the question is: which resin is more cost effective?

***Polystyrene Resins***

Anion	$\alpha_{Cl^-}^X$
$ClO_4^-$	150
$SO_4^{2-}$	11
$NO_3^-$	3
$Cl^-$	1

***Polyacrylic Resins***

Anion	$\alpha_{Cl^-}^X$
$SO_4^{2-}$	15
$ClO_4^-$	4.5
$NO_3^-$	2
$Cl^-$	1



## General Scope of Work

- ◆ Bench-Scale testing to:
  - Evaluate three IX resins (two polystyrene & one polyacrylic resins)
  - Characterize perchlorate breakthrough
  - Evaluate regeneration efficiency of each resin
  - Identify conditions for pilot testing
  
- ◆ Pilot-Scale testing to:
  - Demonstrate performance of three selected resins
  - Operate under full-scale operating conditions
  - Validate bench-scale results
  - Demonstrate biological removal of perchlorate from spent brine
  - Prepare reconnaissance-level cost estimate for full-scale implementation of IX resins for perchlorate removal



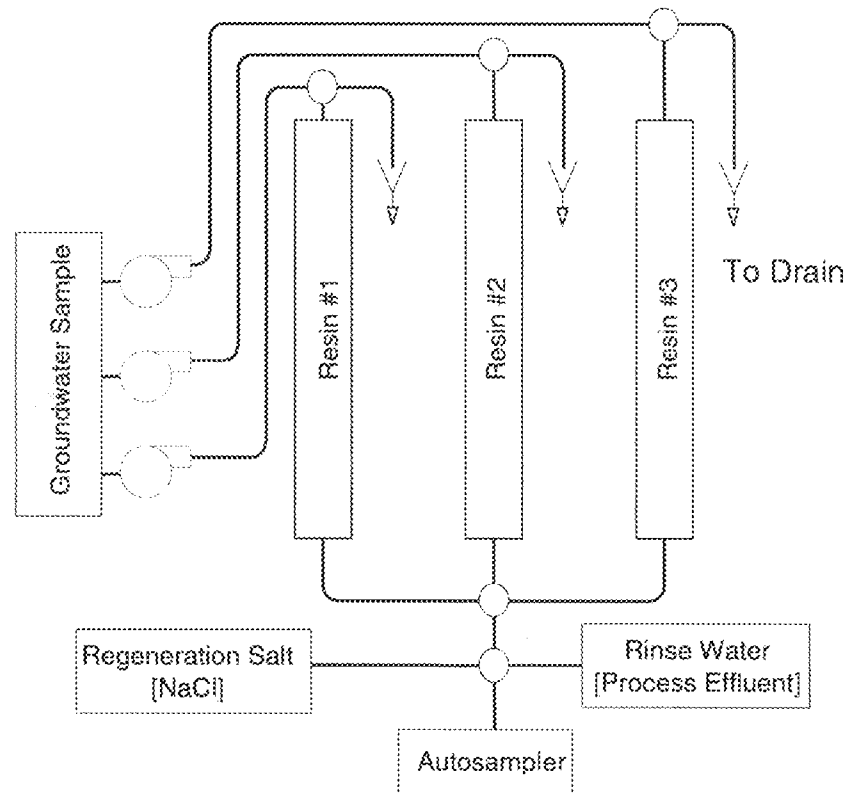
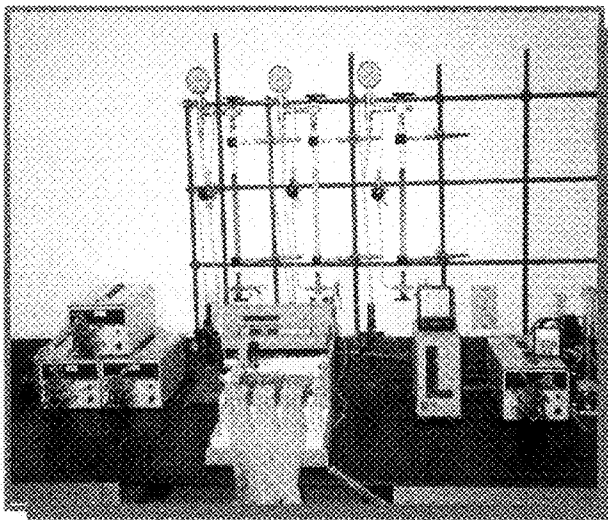
# Bench-Scale Testing



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## Outline of Bench-Scale Testing

- ◆ Groundwater Quality
- ◆ Resins Evaluated
- ◆ Operating Parameters
- ◆ Experimental Results
- ◆ Evaluation of Salt Loading Rate
- ◆ Results of Salt Loading Rate Evaluation
- ◆ Summary of Bench-Scale Results



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## Groundwater Quality During Bench-Scale Testing

*Groundwater was obtained from the City of Azusa's Well #9*

<i>Parameter</i>	<i>Unit</i>	<i>Value</i>
Alkalinity	mg/L as CaCO <sub>3</sub>	200
pH	-	8.0
Nitrate	mg/L as N	9.0
Sulfate	mg/L	55
Perchlorate	ug/L	200*
TOC	mg/L	1.2

\* Spiked Perchlorate Level



## Strong-Base Resins Evaluated During Bench-Scale Testing

### **IRA400** **Rohm & Haas Co.**

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- ◆ Strongly hydrophobic
- ◆ Polystyrene resin
- ◆ High affinity for Perchlorate
- ◆ Capacity = 1.4 meq/mL
- ◆ Selectivity ( $\text{ClO}_4^-$  to  $\text{Cl}^-$ ) = 150
- ◆ Difficult to regenerate

### **ASB-2** **Sybron Chemicals Inc.**

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- ◆ Hydrophobic
- ◆ Polystyrene resin
- ◆ High affinity for Perchlorate
- ◆ Capacity = 1.4 meq/mL
- ◆ Selectivity ( $\text{ClO}_4^-$  to  $\text{Cl}^-$ ) = 150
- ◆ Difficult to regenerate

### **IRA458** **Rohm & Haas Co.**

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- ◆ Strongly hydrophilic
- ◆ Polyacrylic resin
- ◆ Low(er) affinity for Perchlorate
- ◆ Capacity = 1.25 meq/mL
- ◆ Selectivity ( $\text{ClO}_4^-$  to  $\text{Cl}^-$ ) = 4.5
- ◆ Easy to regenerate with NaCl



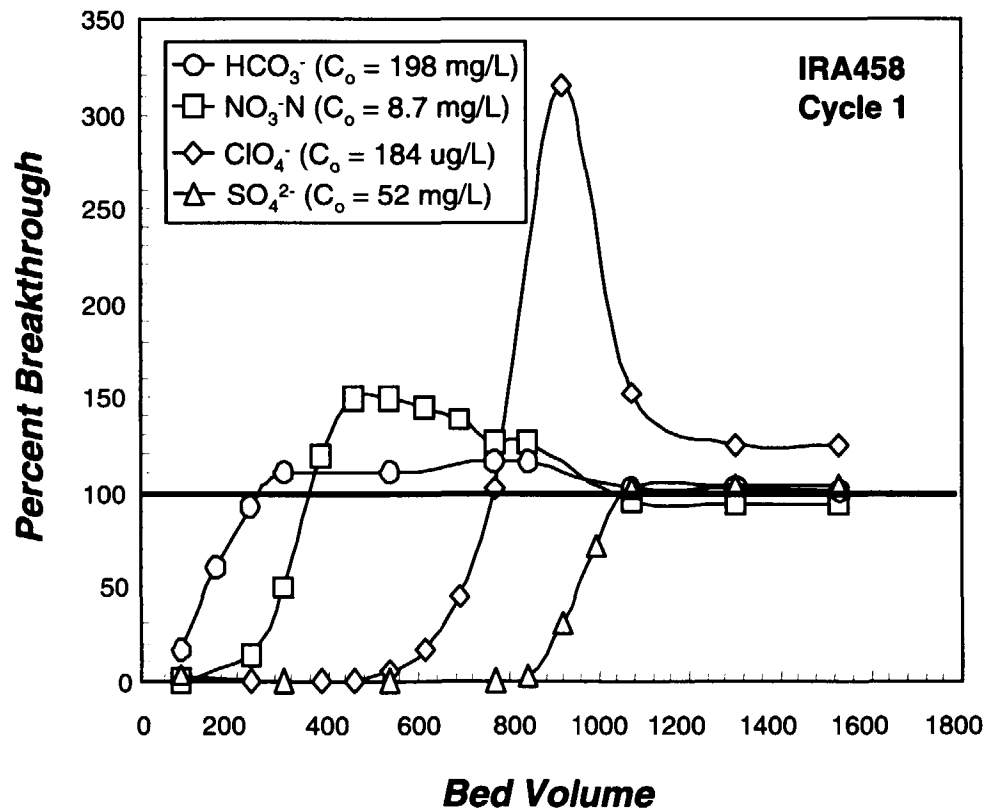


## Bench-Scale Operating & Regeneration Conditions

<b><i>Parameter</i></b>	<b><i>Unit</i></b>	<b><i>Value</i></b>
Operational mode	-	Concurrent
EBCT	min	1.5
Service Loading Rate	gpm/ft <sup>3</sup>	4.8
Flow Rate per Column	mL/min	13
Resin Volume per Column	mL	20
Regenerent Type	-	NaCl
Regenerent Strength	%	6%
	mg/L	60,000
Salt Loading Rate	lbs/ft <sup>3</sup>	15
Regeneration & Rinse Flowrate	mL/min	3.5
Regeneration Volume	Bed Volumes (BVs)	4
Rinse Volume	BVs	1.8



## Polyacrylic IRA458 Resin - First Cycle

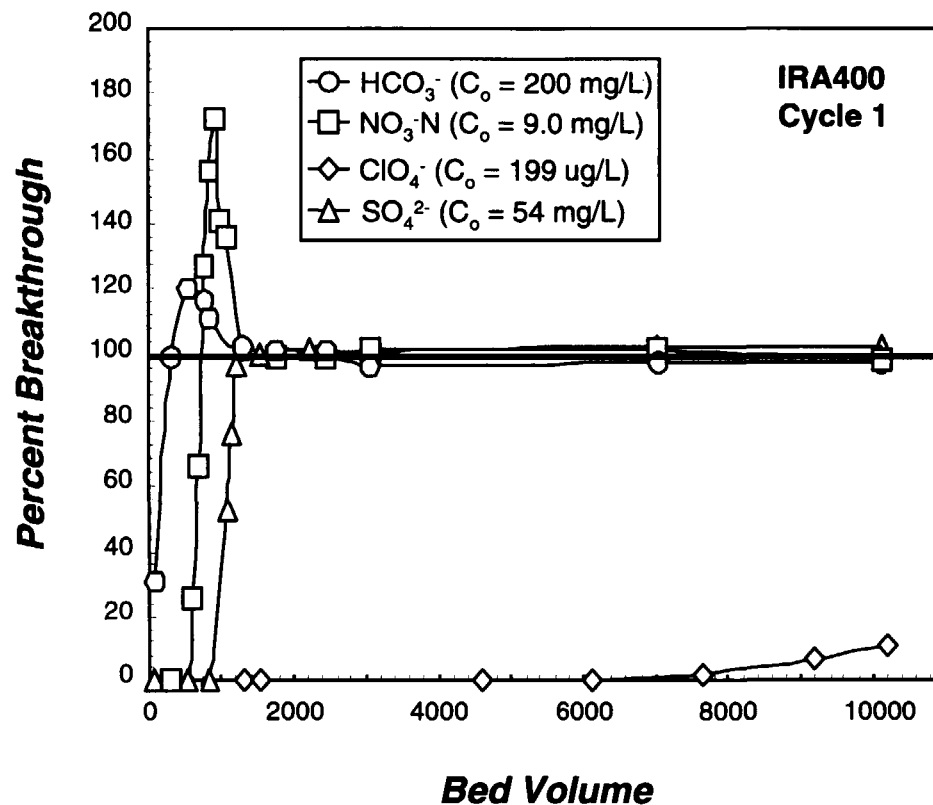


- ◆ Perchlorate breakthrough occurs after nitrate and before sulfate
- ◆ Perchlorate breakthrough occurred at approximately 450 Bed Volumes (BVs)
- ◆ A chromatographic effect is clearly observed in which perchlorate breakthrough pushes the nitrate effluent concentration to higher than its influent value. Similarly, sulfate breakthrough pushes perchlorate effluent concentration to as high as three times its influent value
- ◆ As such, if the nitrate chromatographic peak is greater than its MCL (10 mg/L as N), then the run will have to be terminated at nitrate breakthrough.
- ◆ This would greatly reduce the run time, and thus increase cost



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## Polystyrene IRA400 Resin - First Cycle

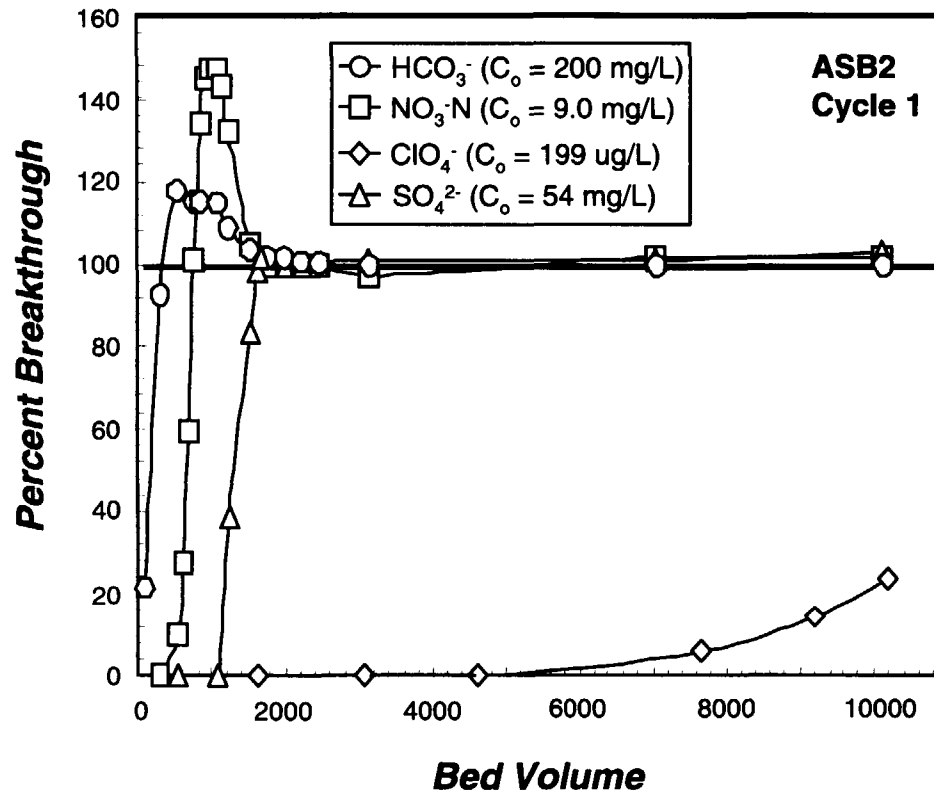


- ◆ Perchlorate breakthrough occurs long after sulfate breakthrough.
- ◆ Perchlorate breakthrough occurred at approximately 7,500 bed volumes.
- ◆ A chromatographic effect is also observed in which sulfate breakthrough pushes the nitrate effluent concentration to higher than its influent value.



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## Polyacrylic ASB2 Resin - First Cycle

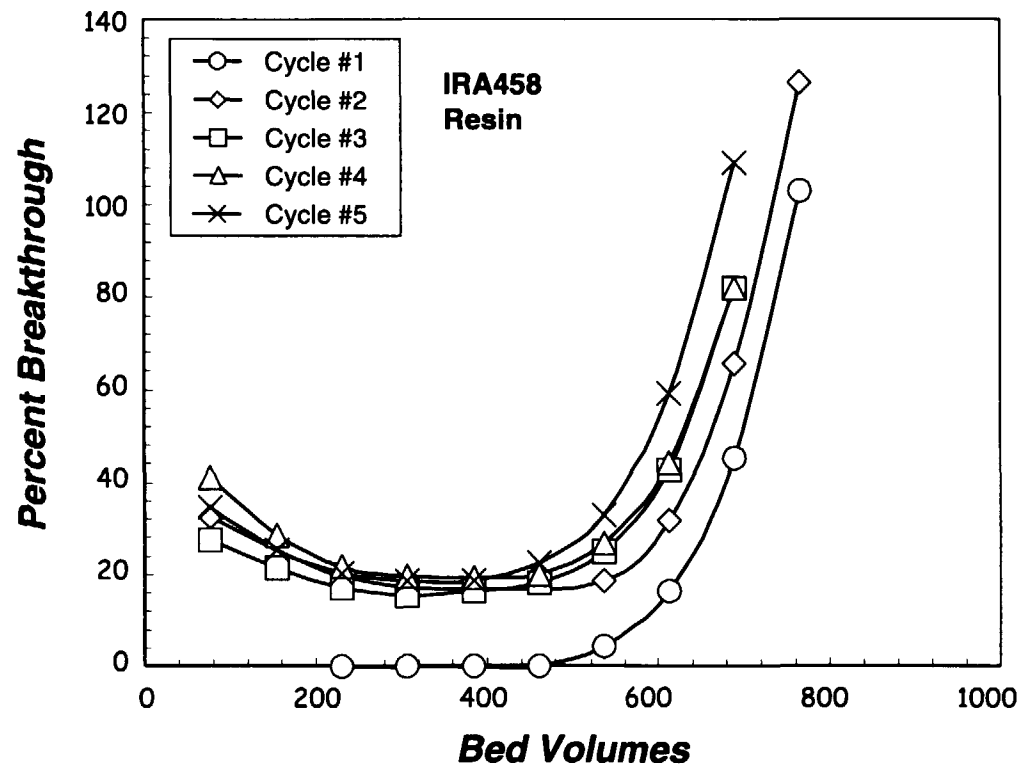


- ◆ Perchlorate breakthrough occurs long after sulfate breakthrough.
- ◆ Perchlorate breakthrough occurred at approximately 6,000 bed volumes.
- ◆ A chromatographic effect is also observed in which sulfate breakthrough pushes the nitrate effluent concentration to higher than its influent value.



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## Polyacrylic IRA458 Resin - Subsequent Cycles

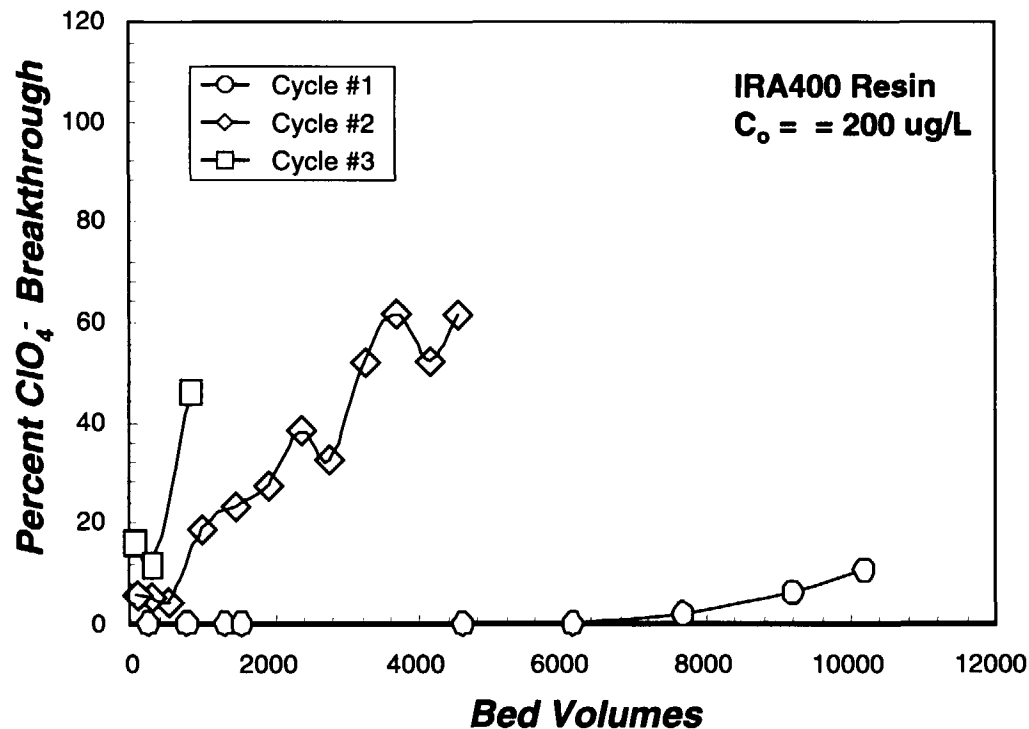


- ◆ The data show excessive “leakage” of perchlorate immediately after starting the runs.
- ◆ Leakage is defined as the immediate appearance of perchlorate ion in the IX column effluent upon startup.
- ◆ This suggests ineffective regeneration of the resin.
- ◆ Note that the column was operated in a co-current mode and regenerated at a salt loading rate of 15 lbs/ft<sup>3</sup>.



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## Polystyrene IRA400 Resin - Subsequent Cycles

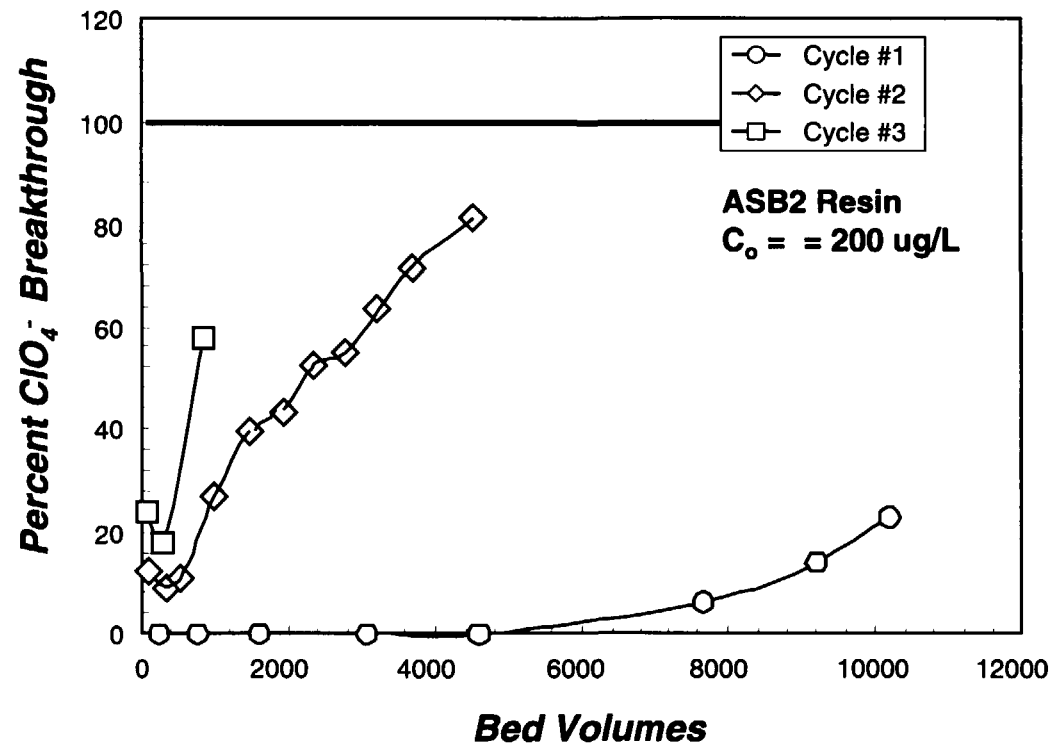


- ◆ Two important observations are made:
  - The regeneration conditions were vastly inefficient in recovering the capacity of the resin
  - Significant “leakage” of perchlorate occurred at the beginning of each subsequent run
- ◆ Note that the column was operated in a co-current mode and regenerated at a salt loading rate of 15 lbs/ft<sup>3</sup>.



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## Polystyrene ASB2 Resin - Subsequent Cycles

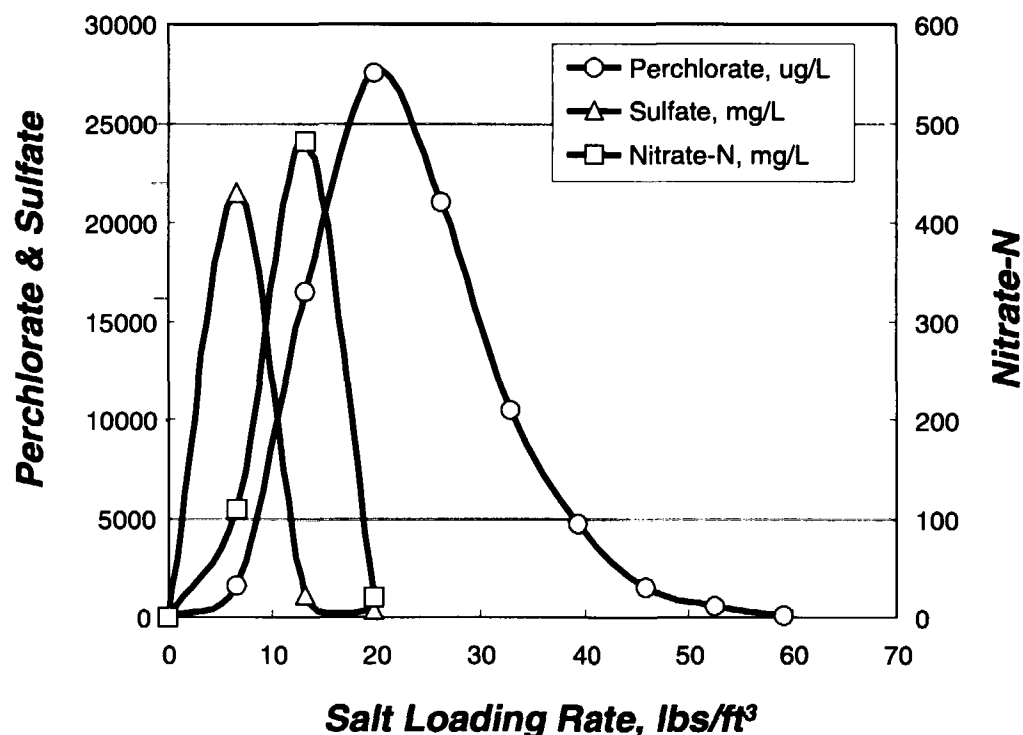


- ◆ Similar to IRA400 resin, two important observations are made:
  - The regeneration conditions were vastly inefficient in recovering the capacity of the resin
  - Significant “leakage” of perchlorate occurred at the beginning of each subsequent run
- ◆ Note that the column was operated in a co-current mode and regenerated at a salt loading rate of 15 lbs/ft<sup>3</sup>.



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## Regeneration Efficiency of IRA-458 Resin [after 13 regenerations at a salt loading rate of 15 lbs/ft<sup>3</sup>]



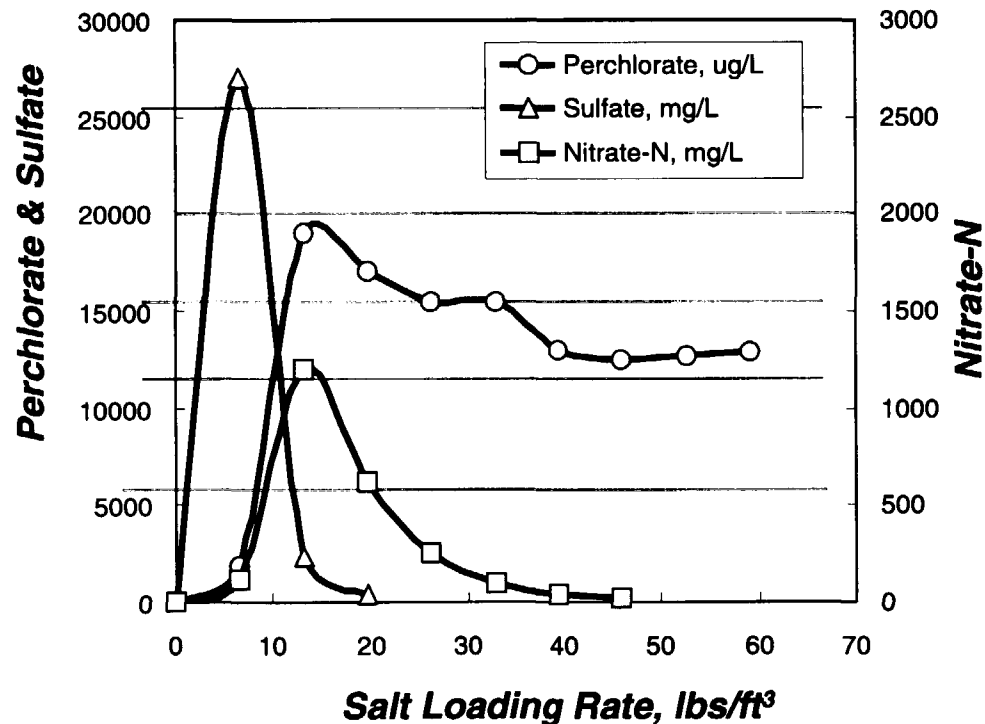
- ◆ The results show that during regeneration, sulfate elutes first, followed by nitrate and then perchlorate.
- ◆ Regeneration with 15 lbs/ft<sup>3</sup> is sufficient to remove all the sulfate and a large portion of the nitrate.
- ◆ However, the regeneration results show that only a fraction of the perchlorate is removed with a salt loading rate of 15 lbs/ft<sup>3</sup>.
- ◆ The results indicate that a salt loading rate between 30 and 45 lbs/ft<sup>3</sup> may be required to ensure that a significant portion of the perchlorate adsorbed on the IRA458 resin is removed.
- ◆ The results also indicate that regeneration of IRA458 resin with salt can fully recover the capacity of the resin for perchlorate.



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## Regeneration Efficiency of IRA400 Resin [after 3 regenerations at a salt loading rate of 15 lbs/ft<sup>3</sup>]



- ◆ During regeneration of IRA400 resin, sulfate elutes first, followed by nitrate and perchlorate.
- ◆ The results show that a salt loading rate of 15 lbs/ft<sup>3</sup> removes all the sulfate, but only half the nitrate adsorbed on the resin.
- ◆ The regeneration results show that a salt loading rate of 15 lbs/ft<sup>3</sup> removes only a small fraction of the perchlorate adsorbed on the resin.
- ◆ The results indicate that a salt loading rate as high as 60 lbs/ft<sup>3</sup> is not sufficient to fully recover the capacity of the IRA400 resin for perchlorate.



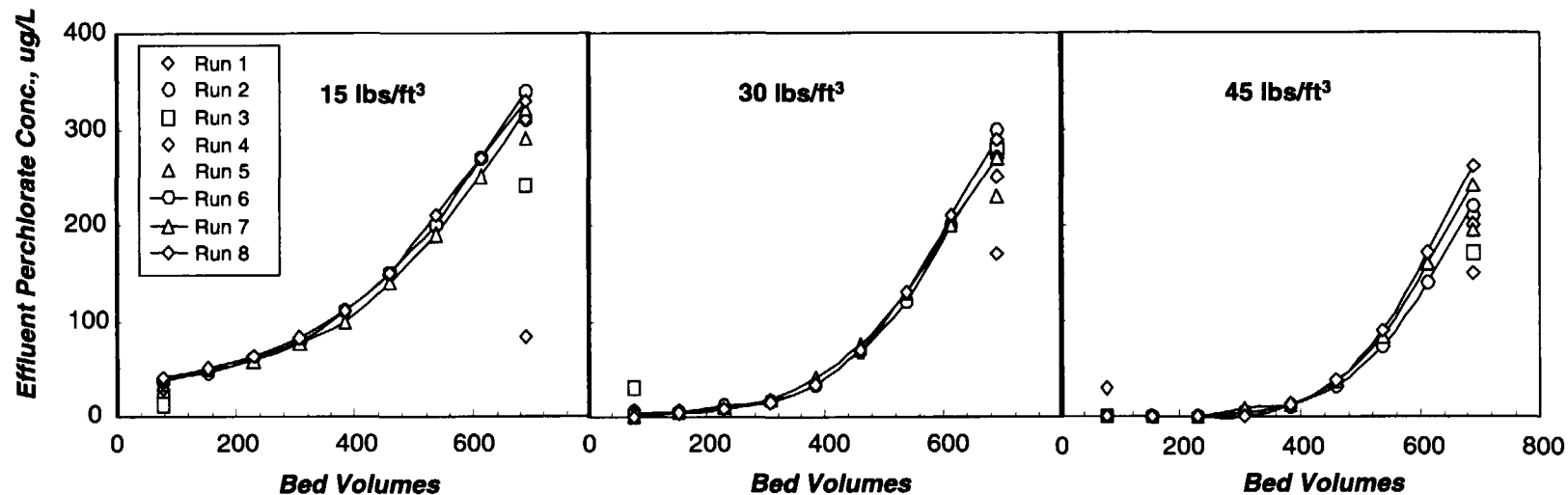
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## **Evaluation of the Impact of the Salt Loading Rate on the Regeneration Efficiency of IRA458 Resin**

- ◆ The three columns were refilled with fresh IRA458 resin
- ◆ The columns were regenerated with salt loading rates of 15, 30, and 45 lbs/ft<sup>3</sup>
- ◆ Column operation was changed from a co-current to a counter-current mode
- ◆ Each column was operated for 5 consecutive runs
- ◆ The elution curves of each anion during the 5th regeneration cycle was determined
- ◆ The columns were then operated and sampled for three consecutive runs



## Impact of Salt Loading Rate on the Regeneration Efficiency of IRA458 Resin



- ◆ Perchlorate leakage was persistent at 15 lbs/ft³, but decreased as the salt loading rate increased to 30 and 45 lbs/ft³ (influent perchlorate concentration was approximately 200 ug/L)
- ◆ Breakthrough of perchlorate was delayed to 150 BVs with a salt loading rate of 30 lbs/ft³, and to approximately 300 bed volumes at a salt loading rate of 45 lbs/ft³.
- ◆ However, it should be noted that full perchlorate breakthrough was allowed, whereas full-scale systems would be operated till perchlorate effluent concentration reaches the operational target effluent concentration.
- ◆ Terminating the run at operational perchlorate breakthrough levels would result in improved perchlorate regeneration, and thus lower perchlorate leakage.



## Summary of Bench-Scale Testing Results

- ◆ Strong-base anion exchange resins are effective for the removal of perchlorate from groundwater, but the process requires optimization.
- ◆ Polystyrene resins have higher affinity for perchlorate, but are difficult to regenerate.
- ◆ Polyacrylic resins have moderate affinity for perchlorate and can be effectively regenerated.
- ◆ Perchlorate leakage occurs at a salt loading rate of 15 lbs/ft<sup>3</sup>.
- ◆ A salt loading rate of 30 lbs/ft<sup>3</sup> or greater may be required to eliminate leakage.



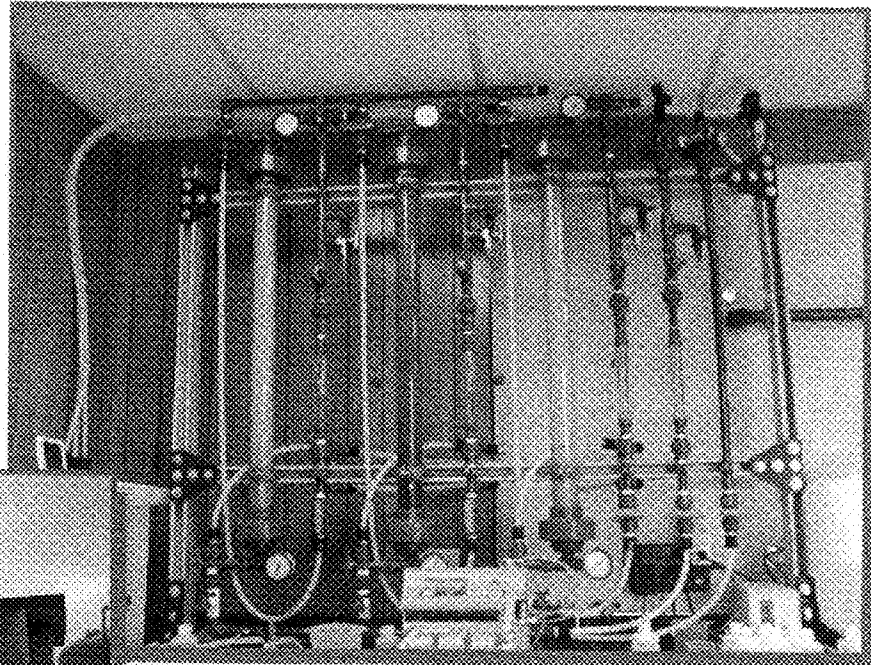
# Pilot-Scale Testing



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## Pilot-Scale Testing

- ◆ Groundwater Quality
- ◆ Resins Evaluated
- ◆ Operating Parameters
- ◆ Experimental Results
- ◆ Evaluation of Higher Salt Concentration
- ◆ Results of Higher Salt Concentration
- ◆ Summary of Pilot-Scale Results



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## Groundwater Quality During Pilot-Scale Testing

- ◆ *All testing was conducted at the Big Dalton Well, Baldwin Park, CA*
- ◆ *Values reported are averages of 36 measurements (except for TOC and Hardness)*

Parameter	Unit	Value
Alkalinity	mg/L as CaCO <sub>3</sub>	122
Hardness	mg/L as CaCO <sub>3</sub>	163
pH	-	7.8
Nitrate	mg/L as N	6.6
Sulfate	mg/L	53
Perchlorate	ug/L	90 - 140*
TOC	mg/L	0.9

\* Natural and spiked levels



## Strong-Base Resins Evaluated During Pilot-Scale Testing

A850 Purolite	ASB-2 Sybron Chemicals Inc.	IRA458 Rohm & Haas Co.
<ul style="list-style-type: none"> <li>◆ hydrophilic</li> <li>◆ Polyacrylic resin</li> <li>◆ Moderate affinity for perchlorate</li> <li>◆ Capacity = 1.25 meq/mL</li> <li>◆ Selectivity (<math>\text{ClO}_4^-</math> to <math>\text{Cl}^-</math>) = 4.5</li> <li>◆ Easy to regenerate</li> </ul>	<ul style="list-style-type: none"> <li>◆ Slightly hydrophobic</li> <li>◆ Polystyrene resin</li> <li>◆ High affinity for perchlorate</li> <li>◆ Capacity = 1.4 meq/mL</li> <li>◆ Selectivity (<math>\text{ClO}_4^-</math> to <math>\text{Cl}^-</math>) = 150</li> <li>◆ Difficult to regenerate</li> </ul>	<ul style="list-style-type: none"> <li>◆ hydrophilic</li> <li>◆ Polyacrylic resin</li> <li>◆ Moderate affinity for perchlorate</li> <li>◆ Capacity = 1.25 meq/mL</li> <li>◆ Selectivity (<math>\text{ClO}_4^-</math> to <math>\text{Cl}^-</math>) = 4.5</li> <li>◆ Easy to regenerate with NaCl</li> </ul>





## Pilot-Scale Operating & Regeneration Conditions

<b><i>Parameter</i></b>	<b><i>Unit</i></b>	<b><i>Value</i></b>
Operational mode	-	Counter-current
EBCT	min	1.5
Service Loading Rate	gpm/ft <sup>3</sup>	5.0
Flow Rate per Column	gpm	0.30
Resin Volume per Column	ft <sup>3</sup>	0.062
Regenerent Type	-	NaCl
Regenerent Strength	%	3%*
	mg/L	30,000
Salt Loading Rate	lbs/ft <sup>3</sup>	30
Regeneration & Rinse Flowrate	gpm	0.16
Regeneration Volume	Bed Volumes (BVs)	16
Rinse Volume	BVs	2 to 6**

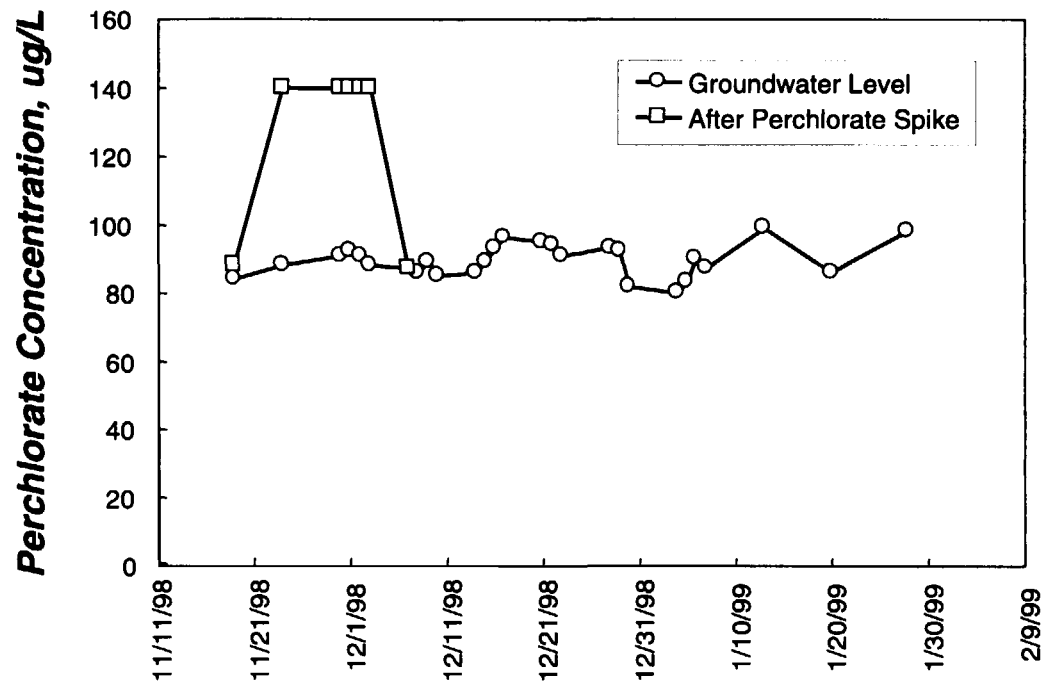
\* Salt strength was set at 3% due to the need to conduct biological testing on the brine

\*\* Each column was rinsed until the effluent conductivity decreased to less than 700 umho/cm



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## Perchlorate Level in the Groundwater



- ◆ The perchlorate level was initially believed to be less than 20 ug/L. As such, the plan was to spike the influent water with approximately 50 ug/L perchlorate.
- ◆ However, after the first three weeks of operation, it was apparent that the perchlorate level in the groundwater had risen to approximately 90 ug/L.
- ◆ As such, on 12/7/98, the perchlorate spiking was terminated, and the influent perchlorate concentration remained between 80 and 100 ug/L throughout the rest of the testing period.



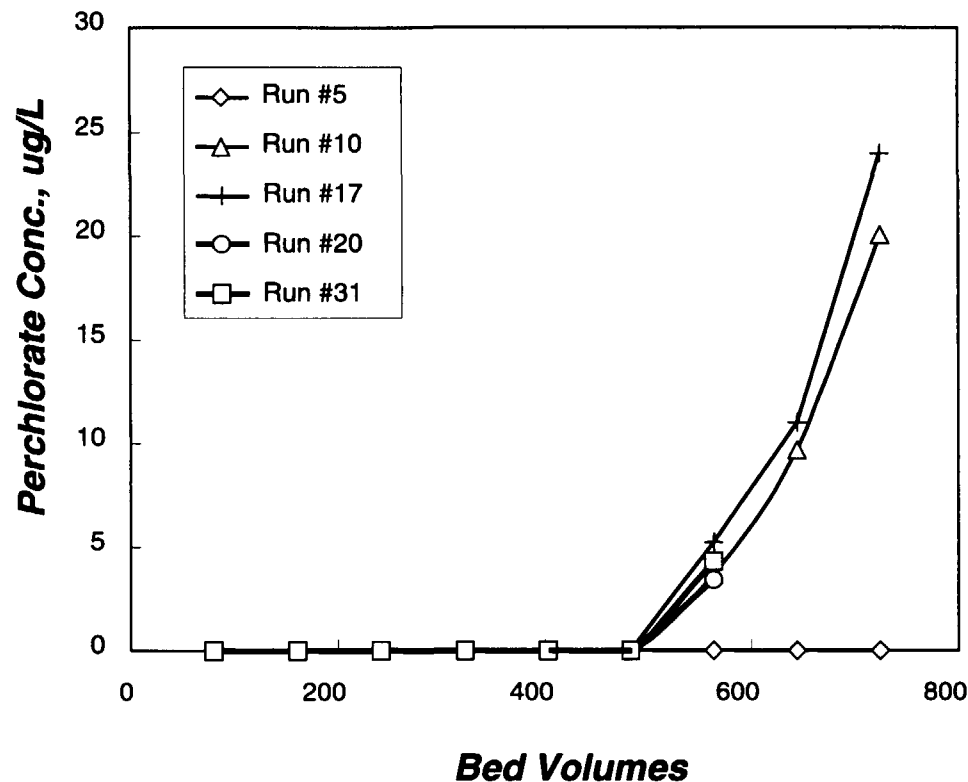
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## Pilot Plant Operational Strategy

- ◆ The three columns were operated in parallel for a period of 10 weeks.
- ◆ Each column was initially operated for a period of 725 bed volumes, at which time the run was automatically terminated, and the resin was regenerated. Based on the bench-scale results, this run time was predetermined to be the time at which perchlorate breakthrough occurs.
- ◆ Breakthrough was defined as exceeding the perchlorate minimum reporting limit (MRL) of 4 ug/L.
- ◆ If the effluent of a column consistently exceeded the MRL at the 750 BVs run-time, the run time was reduced to maintain the perchlorate concentration in the effluent at or below the MRL.
- ◆ The effluent of each column was monitored using an auto-sampler.
- ◆ The pilot plant was attended between 7:30 AM to 3:00 PM, Monday through Friday. If a run terminated between 3:00 PM and 7:30 AM the following day, the resin was left idle until the next morning when it was regenerated.
- ◆ On Fridays, the columns were regenerated and rinsed before they were allowed to stand idle until they were restarted on the following Monday.
- ◆ All columns were regenerated with a 3% NaCl solution at a loading rate of 30 lbs/ft<sup>3</sup> with the following exceptions:
  - After Cycle #23, the salt strength was increased to 4%.
  - During the last week, the salt loading rate for the last four runs was decreased to 20 lbs/ft<sup>3</sup>.
- ◆ Each column was rinsed with product water collected at the beginning of the preceding run.
- ◆ Rinsing was maintained until the conductivity of the effluent decreased to below 700 umho/cm in order to simulate full-scale operational conditions.



## Removal of Perchlorate with Rohm & Haas' IRA458 Resin

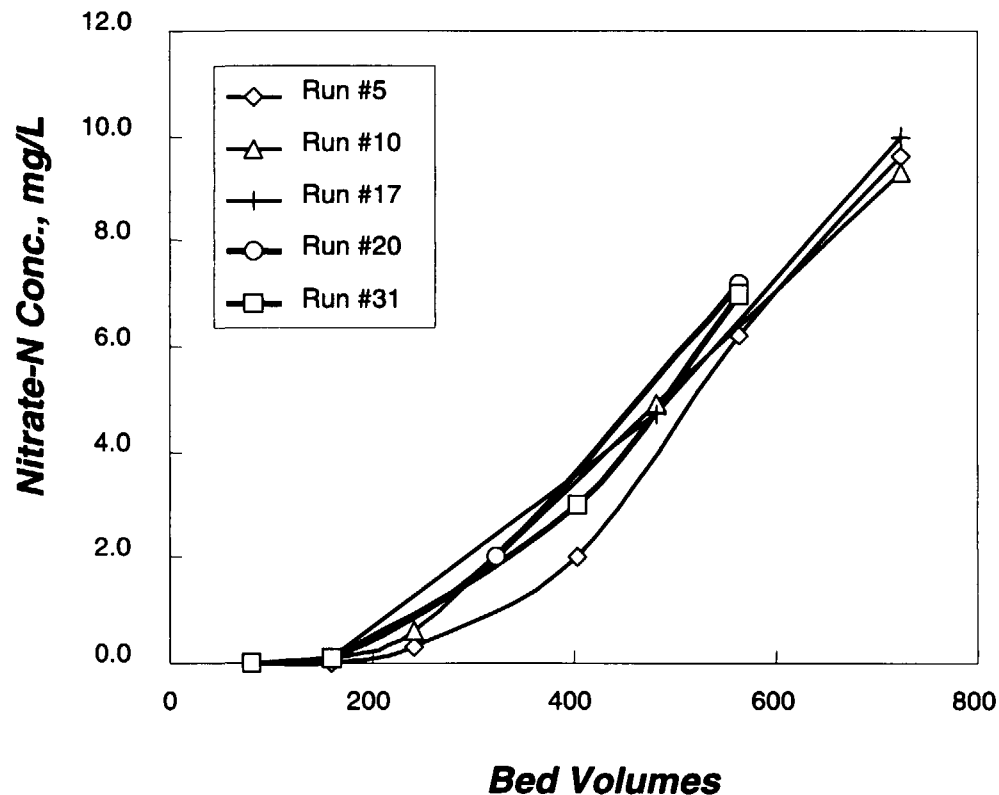


- ◆ The resin was operated for a total of 31 cycles at 30 lbs/ft<sup>3</sup> salt regeneration rate.
- ◆ Initially, perchlorate breakthrough occurred at 725 BVs, but later it started occurring at 560 BVs.
- ◆ As such, after 17 cycles, the run-time was reduced to 560 BVs.
- ◆ At 560 BVs, perchlorate was consistently reduced to less than 5 ug/L.
- ◆ Perchlorate breakthrough was reproducible over the entire 31 cycles, which suggests that full regeneration of the resin was accomplished with the salt loading rate of 30 lbs/ft<sup>3</sup>.



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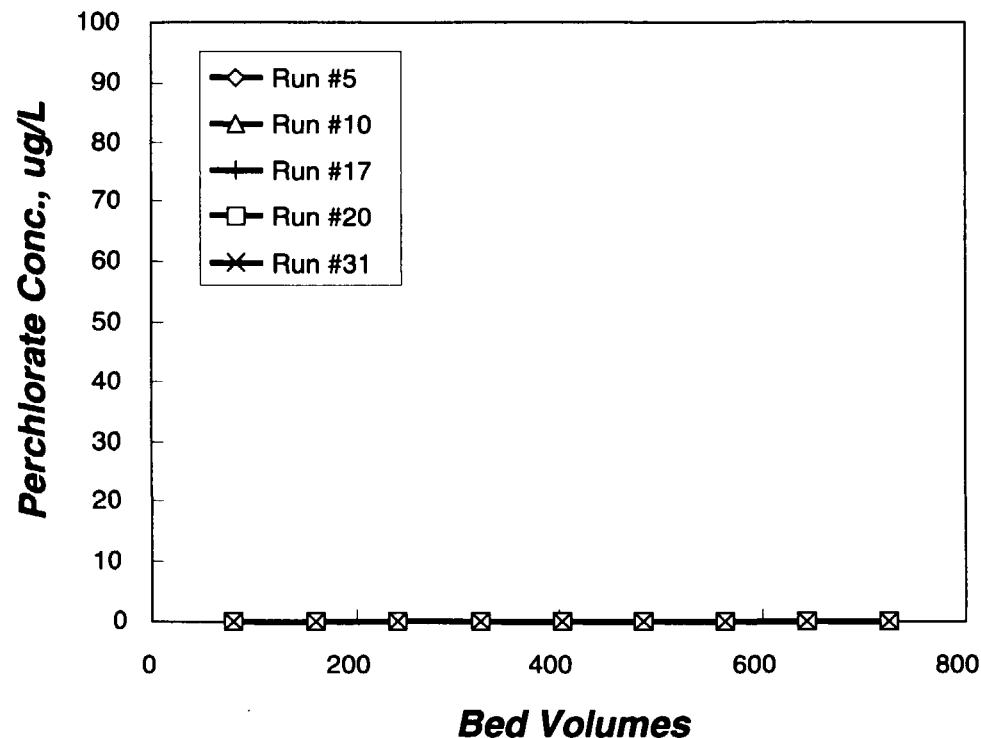
## Removal of Nitrate with Rohm & Haas' IRA458 Resin



- ◆ During the first 17 cycles, the maximum nitrate concentration reached (at 725 bed volumes) was 10 mg/L as N.
- ◆ After the run time was reduced to 560 bed volumes to control perchlorate breakthrough, the maximum nitrate concentration was approximately 8 mg/L as N.
- ◆ The nitrate breakthrough profile was fairly reproducible over a total of 31 cycles.



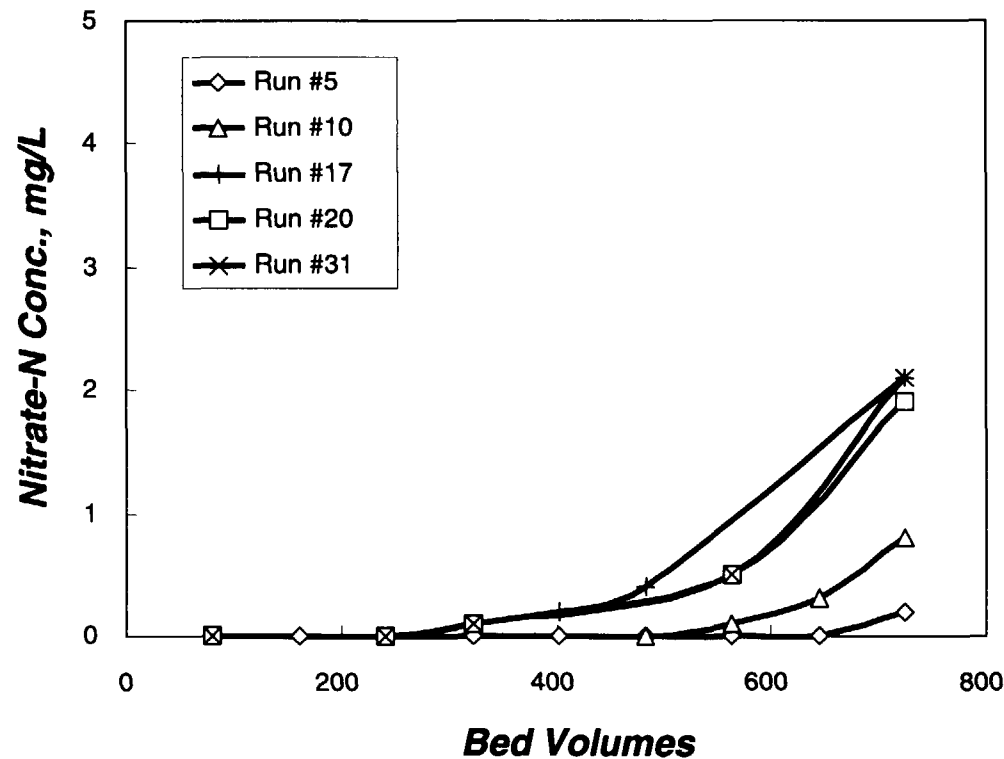
## Removal of Perchlorate with Sybron's ASB2 Resin



- ◆ All perchlorate values in the effluent of the ASB2 columns were non-detectable (< 4 ug/L) for all 31 cycles.
- ◆ However, based on the perchlorate elution results during regeneration (discussed later), the resin was losing part of its capacity with each cycle.
- ◆ Although no breakthrough occurred in 31 cycles when the resin was operated for 750 bed volumes during each cycle, it is not certain whether long-term operation will result in early breakthrough of perchlorate.



## Removal of Nitrate with Sybron's ASB2 Resin

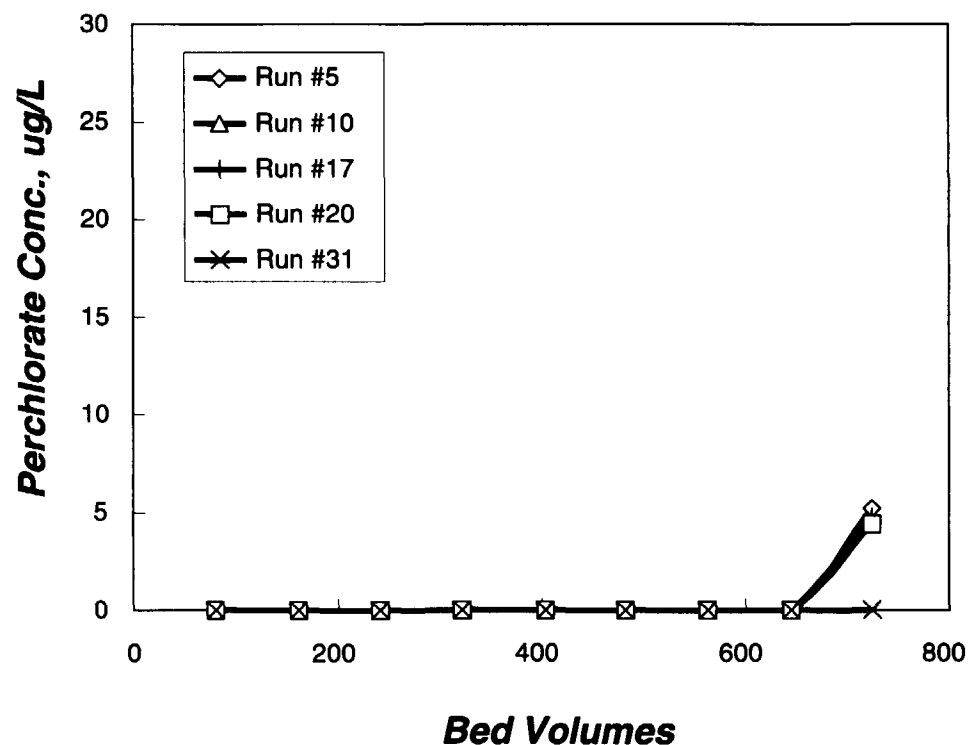


- ◆ During all 31 runs, the nitrate concentration in the effluent did not exceed 2 mg/L as N.
- ◆ The results show that the resin capacity for nitrate decreased with time. However, the results seem to indicate that no decrease in capacity occurred between runs 17 and 31.



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## Removal of Perchlorate with Purolite's A850 Resin



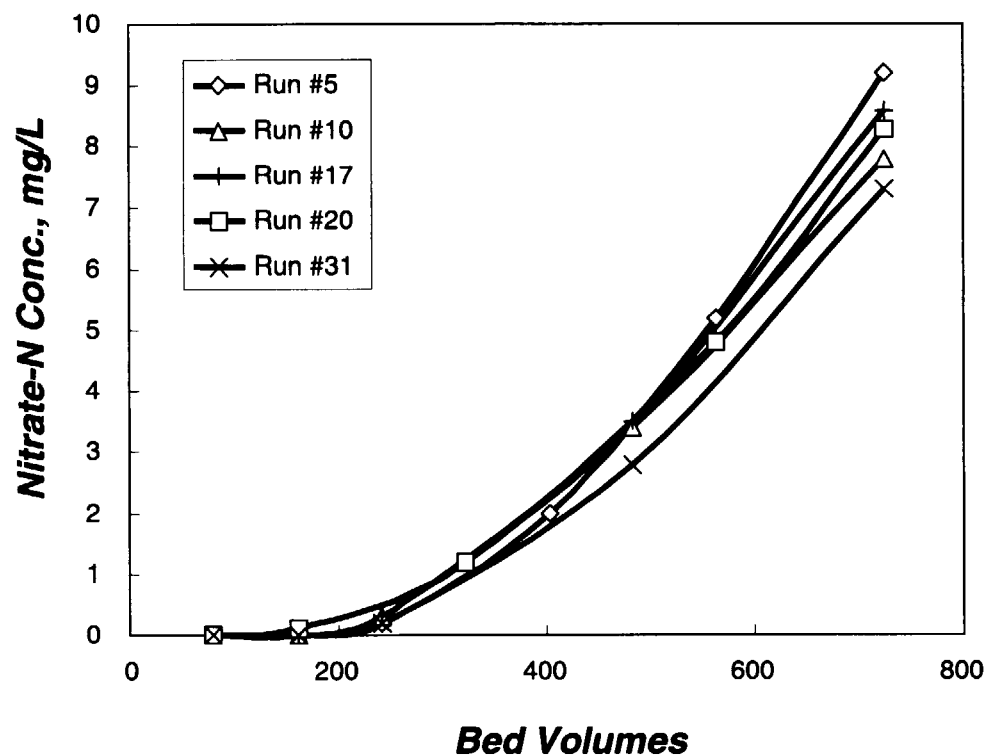
- ◆ The resin was operated for a total of 31 cycles at 30 lbs/ft<sup>3</sup> salt regeneration rate.
- ◆ Perchlorate breakthrough occurred consistently at 725 bed volumes.
- ◆ Perchlorate breakthrough was very reproducible over the 31 cycles, which implies that full regeneration of the resin was accomplished with the salt loading rate of 30 lbs/ft<sup>3</sup>.



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## Removal of Nitrate with Purolite's A850 Resin

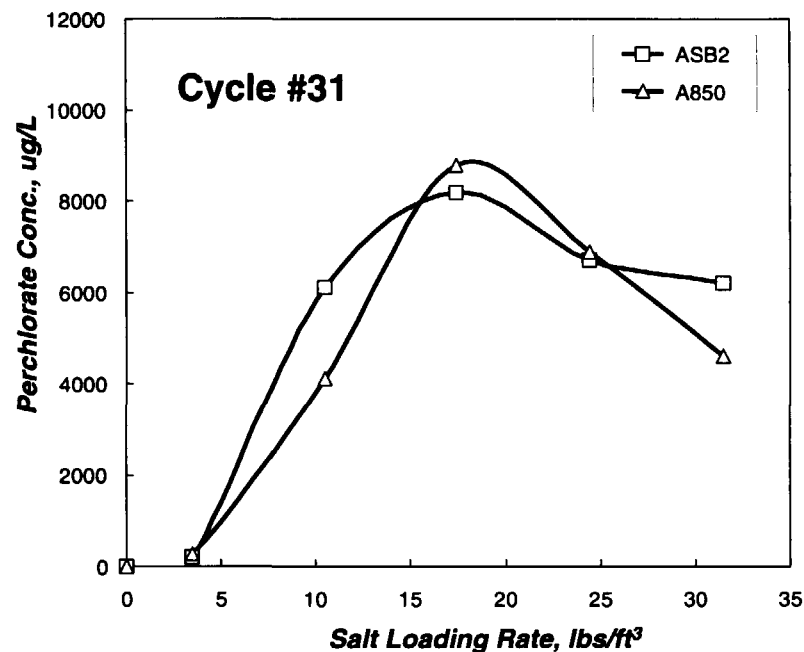
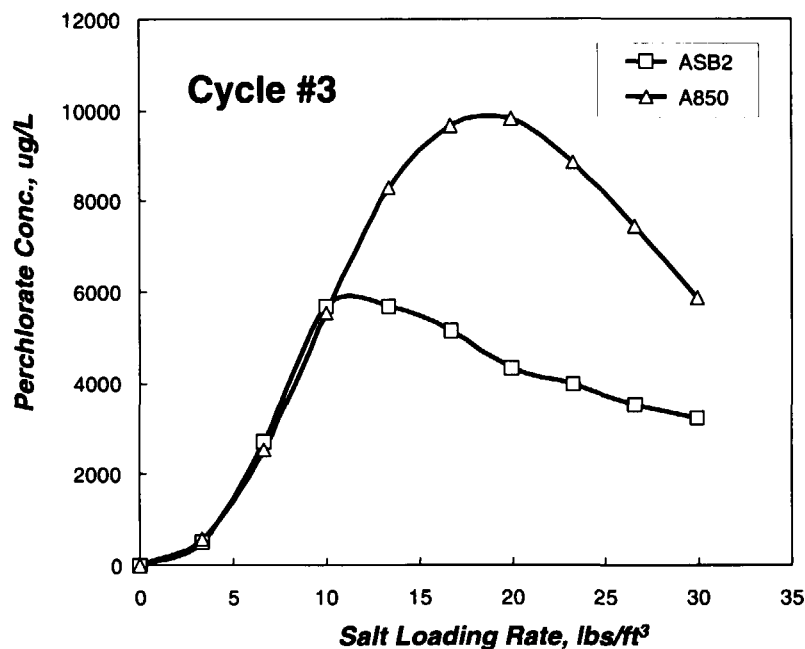


- ◆ During all 31 cycles, the maximum nitrate concentration reached (at 725 bed volumes) was 9 mg/L as N.
- ◆ The nitrate breakthrough profile was fairly reproducible over a total of 31 cycles. This confirms the earlier conclusion that 30 lbs/ft<sup>3</sup> salt loading rate achieved full regeneration of the resin capacity.



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## Impact of Cycle # on Regeneration Efficiency



- ◆ Although virtually the same amount of perchlorate adsorbed on the ASB2 and A850 resins, only partial recovery of the ASB2 resin capacity occurred after Cycle #3 compared to that of the A850 resin.
- ◆ However, the results suggest that after 31 cycles the regeneration efficiency of ASB2 resin was virtually the same as that of A850 resin, indicating that the ASB2 resin may have reached a steady-state condition.



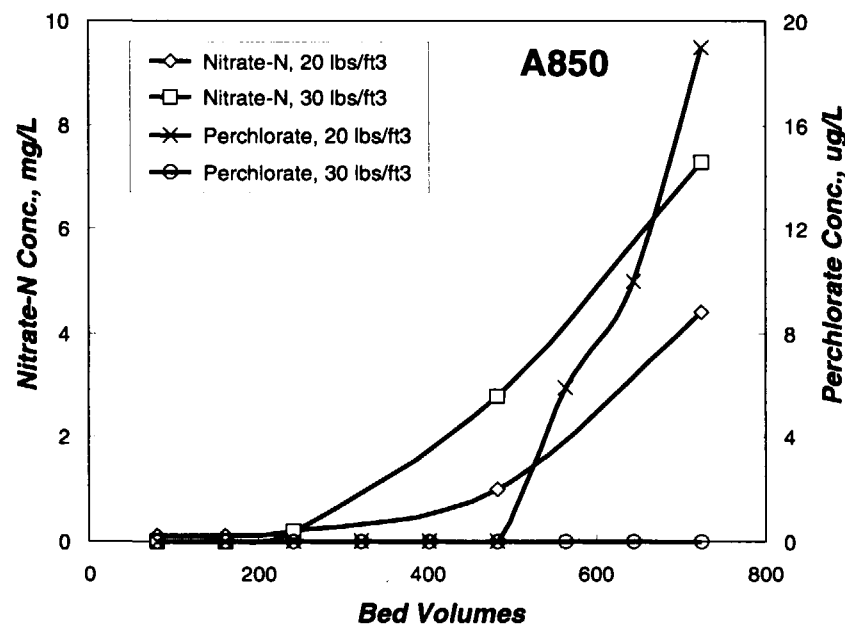
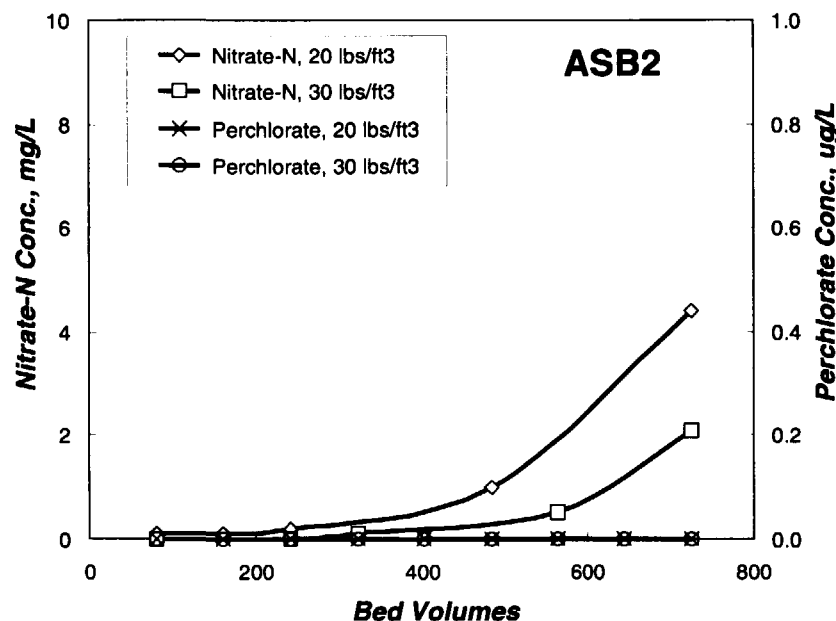
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## Evaluation of the Impact of Salt Loading Rate

- ◆ During the last week of testing, the three resins were regenerated at a salt loading rate of 20 lbs/ft<sup>3</sup> instead of the 30 lbs/ft<sup>3</sup> used throughout the first 9 weeks.
- ◆ Each resin went through four cycles of service and regeneration with 20 lbs/ft<sup>3</sup>.
- ◆ The breakthrough profile of perchlorate, nitrate, and sulfate was monitored in the fourth and last run.
- ◆ In addition, the elution curve of perchlorate, nitrate, and sulfate during the final regeneration was also monitored.



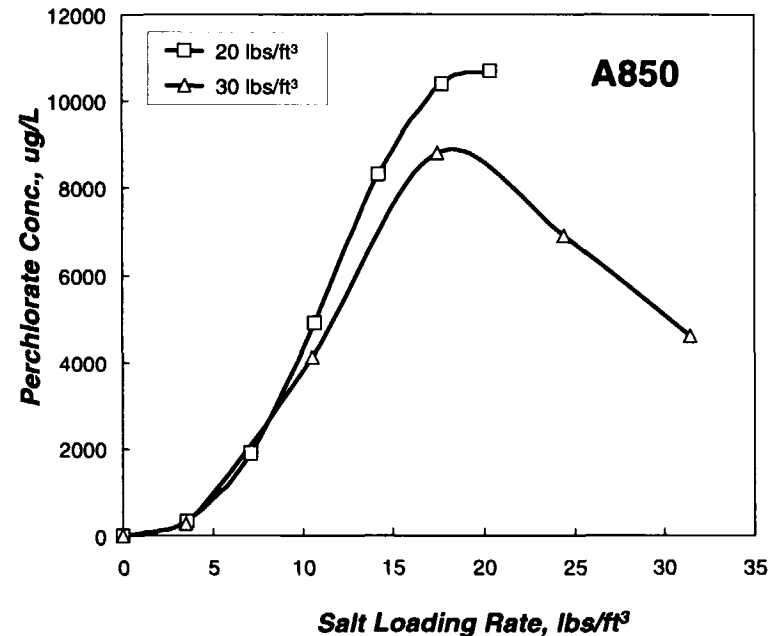
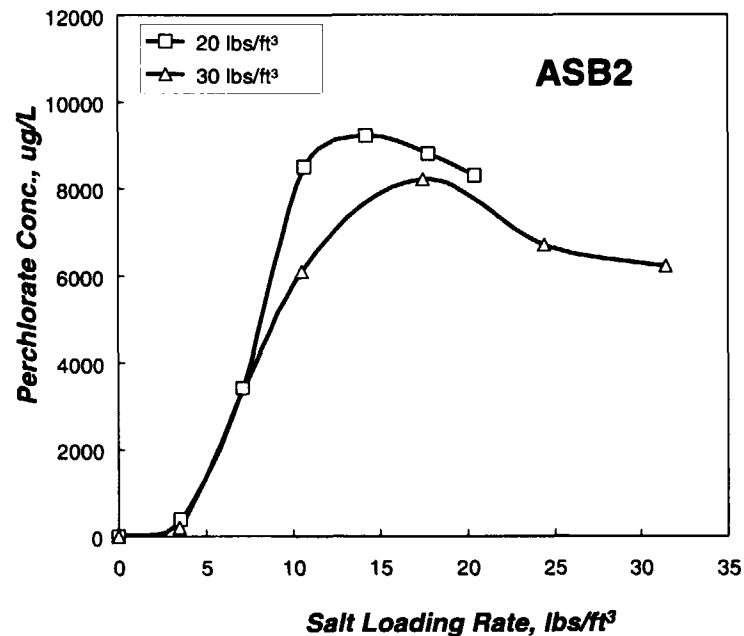
## Impact of Salt Loading Rate on Process Performance



- ◆ ASB2 Resin: Reducing the salt loading rate from 30 lbs/ft³ to 20 lbs/ft³ did not impact the perchlorate breakthrough (within a 725-BV run), but reduced the resin capacity for nitrate.
- ◆ A850 Resin: Reducing the salt loading rate from 30 lbs/ft³ to 20 lbs/ft³ reduced the perchlorate breakthrough time from 725 BVs to approximately 500 BVs. Similarly, the capacity of the resin for nitrate also decreased.
- ◆ For ASB2 resin, a salt loading rate of 20 lbs/ft³ may be feasible. However, for the A850 resin, there appears to be no benefit to going from 30 lbs/ft³ to 20 lbs/ft³.



## Impact of Salt Loading Rate on Regeneration Efficiency



- ◆ The results show that increasing the salt loading rate from 20 to 30 lbs/ft³ removes additional perchlorate off the resin.
- ◆ As such, and considering the results on the previous page, it is believed that a salt loading rate of 30 lbs/ft³ is necessary to achieve good process removal and high efficiency.



## Summary of Pilot-Scale Testing Results

The pilot testing results confirmed the general results obtained from the bench-scale tests, with some additional beneficial information. Here is a summary of the pilot testing results:

- ◆ Three resins were evaluated: Two polyacrylic resins (IRA458 and A850) and one polystyrene resin (ASB2).
- ◆ The columns were run for 32 cycles with regeneration conducted at a salt loading rate of 30 lbs/ft<sup>3</sup>.
- ◆ The columns were regenerated on perchlorate breakthrough, which varied between the three columns:
  - With the IRA458 resin, the perchlorate breakthrough initially occurred at 725 BVs, but subsequently moved to approximately 560 BVs. Therefore, the steady-state run time for IRA 458 was 560 BVs.
  - With the ASB2 resin, perchlorate breakthrough was never experienced. Nevertheless the run time was set at 725 BVs, at which time the resin was regenerated.
  - With the A850 resin, perchlorate breakthrough occurred at 725 BVs in all 32 cycles.
- ◆ Evaluation of the impact of salt loading rate determined that regeneration with 30 lbs/ft<sup>3</sup> was necessary to maintain the efficiency of resin A850. However, the impact of reduced salt loading rate on ASB2 resin performance was not conclusive.



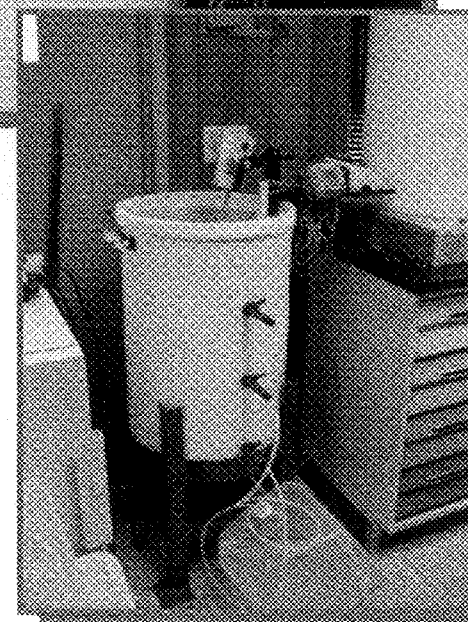
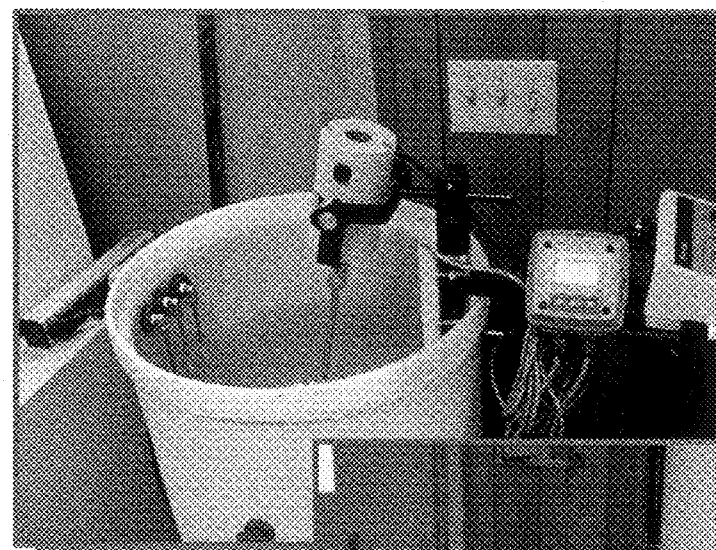
# Brine Biological Treatment



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## Biological Treatment of Spent Brine - Operational Conditions

- ◆ The spent brine and rinse water were mixed and added to a 55-gallon drum equipped with a mixer.
- ◆ Acetic acid was added to the batch solution at a carbon:nitrogen ratio ranging from 0.4:1 to 1.6:1.
- ◆ A bacterial seed was obtained from the Metropolitan Water District of Southern California, which had originated from the aeration basin of a municipal wastewater treatment plant.
- ◆ The batch was continuously mixed and monitored for nitrate and perchlorate concentrations.
- ◆ When the brine solution was to be replenished, the mixer was turned off, the bacterial seed was allowed to settle, the water was decanted, and a fresh spent brine solution and acetic acid were added to the batch.



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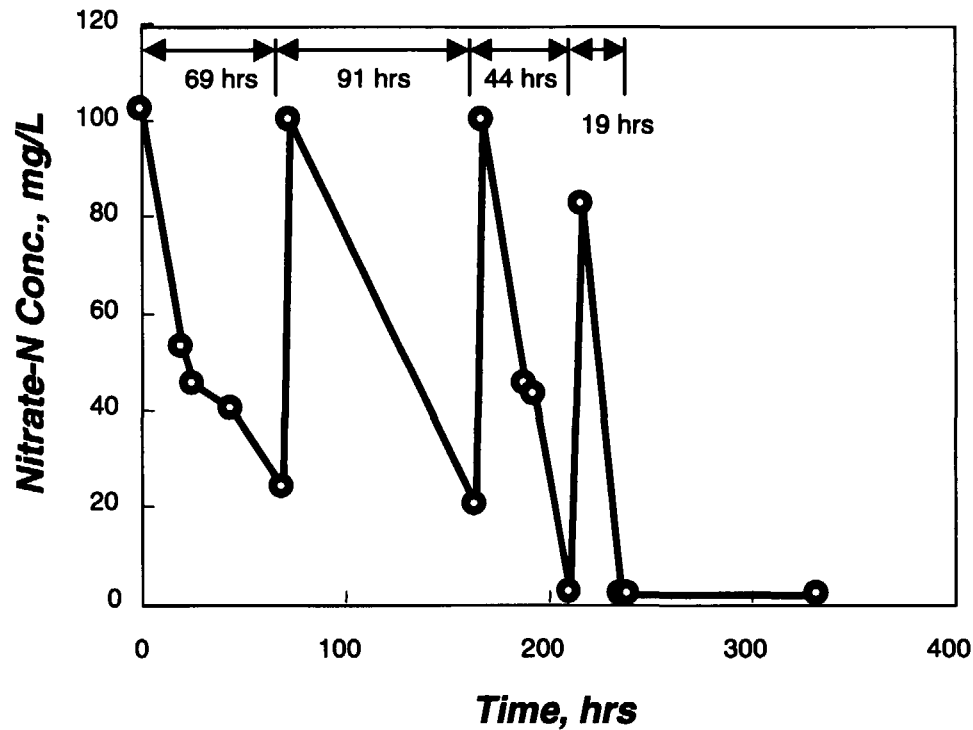
## Quality of the Feed Solution to the Bioreactor

◆ *The spent regeneration brine was mixed with the rinse water*

Parameter	Unit	Value
pH	-	8.6
Nitrate	mg/L as N	89
Sulfate	mg/L	1,592
Perchlorate	mg/L	4.0
Chloride	mg/L as Cl <sup>-</sup>	13,000



## Biological Treatment of Spent Brine - Nitrate Removal



- ◆ The test showed that full reduction of nitrate was achieved by the bacterial seed.
- ◆ The results showed that the acetic acid to nitrate-nitrogen ratio had to exceed the C:N stoichiometric ratio of 1.6:1 to achieve nitrate-N reduction to less than 1 mg/L as N.
- ◆ After the bacterial seed was acclimated to the quality of the brine, the reduction of nitrate from 83 mg/L to 1 mg/L was achieved in less than 19 hours of contact time.



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## **Biological Treatment of Spent Brine - Perchlorate Removal**

- ◆ The perchlorate level in the spent brine ranged from 3.1 to 6.5 mg/L.
- ◆ When blended with the rinse water, the perchlorate level in the bioreactor feed solution averaged approximately 4 mg/L.
- ◆ Over the 4 weeks of biodegradation testing, the bacterial seed was not capable of reducing the perchlorate.
- ◆ However, with a sufficient acclimation period, biological removal of the perchlorate from the brine is highly feasible based on the results obtained by others researchers.
- ◆ The biodegradation of perchlorate in IX brine will be thoroughly evaluated in the upcoming AWWA Research Foundation project to be conducted by the University of Houston and Montgomery Watson.



## Conclusions

- ◆ This feasibility study verified that conventional ion-exchange systems can be effectively and economically used for the removal of perchlorate from contaminated drinking waters
- ◆ The performance of the process is highly dependent on the type of resin used and the quality of the water treated (in terms of the concentrations of other inorganic constituents, specifically nitrate and sulfate)
- ◆ Strong base polyacrylic anion exchange resins are good candidates for perchlorate removal
- ◆ If the ion-exchange resin is operated until perchlorate breakthrough, the results showed that a salt loading rate of 30 lbs/ft<sup>3</sup> may be required for efficient regeneration of polyacrylic resins. This value may decrease if the column run is terminated before perchlorate breakthrough.
- ◆ Based on the tests conducted in this study, Purolite's A850 polyacrylic resin seems to be a good "benchmark" resin to which other resins can be compared in terms of their performance for perchlorate removal.
- ◆ The results of the biological treatment testing for the removal of perchlorate from the spent ion-exchange brine were inconclusive. Extended testing would be required to determine the feasibility of this process.



# Full-Scale Design and Cost Estimate



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## **Conceptual Design of a Full-Scale Ion-Exchange System for Perchlorate Removal**

- ◆ An example full-scale ion-exchange treatment plant is simulated.
- ◆ The plant is sized for a maximum finished water capacity of 2,500 gpm, and an annual average production equal to 90% of capacity.
- ◆ The resin selected for design is Purolite's A850 polyacrylic resin.
- ◆ The plant is designed to have multiple parallel contactors in order to meet the maximum headloss limitation of the resin. Although the blending of the effluents from the parallel contactors would allow for longer run times in each column (and thus higher efficiency), the run time was limited to 725 bed volumes to provide an added design and operational safety factor.
- ◆ One "redundant" contactor is provided. As such, the entire capacity of 2,500 gpm can be treated with one contactor off line.
- ◆ The plant is assumed to treat San Gabriel Basin groundwater with similar quality as that of the Big Dalton well, and is assumed to be located in the vicinity of the non-reclaimed water line (commonly known as the brine line).
- ◆ No brine treatment is assumed in this analysis, and the mixture of spent brine and rinse water is assumed to be discharged into the brine line. It is noted that a 3% salt solution was used during the pilot study because that was the limit for the biological brine-treatment process. However, since no biological treatment is assumed for the full-scale plant, the salt concentration was assumed to be 12%.
- ◆ The cost of the pipeline required to convey the waste flow from the treatment plant to the brine line is not included in this analysis because it is highly dependent on the location of the plant.



## Design Assumptions

Parameter	Value
Design Product Water Capacity	2,500 gpm
Annual Average Flow Rate (@ 90% of Capacity)	2,250 gpm
Water Quality	Identical to Big Dalton Well Water
Minimum Water Temperature	10 °C
Resin Type	Strong-Base Anion Exchange Resin, Polyacrylic, Type I
Maximum Service Loading Rate	5 gpm/ft <sup>3</sup>
BVs to Perchlorate Breakthrough (single column)	725 BVs
Salt Loading Rate (NaCl)	30 lbs/ft <sup>3</sup>
Salt Strength	12%
Rinse Volume	10 BVs
Brine Disposal Strategy	All spent brine and rinse water is disposed off into the brine line
Brine Quality (for estimating brine disposal cost)	
COD	200 mg/L
TSS	80 mg/L
Maximum Headloss Rate	4 psi/ft
Maximum Headloss	20 psi
Redundancy	The plant should be able to treat the entire water flow with one contactor off-line



## Cost Assumptions

Parameter	Value
Resin Unit Cost	\$125/ft <sup>3</sup>
Salt Cost	\$37/ton
Resin Life	5 years
Brine Disposal Cost	Based on LA County Sanitation District Non-reclaimed Line Disposal Cost Equation
Interest Rate	5%
Plant/Equipment Life, years	20
Maintenance Cost (as percent of direct capital cost)	0.5%
No. of Operators	1
Labor Cost	\$30/hr
Operating Schedule	5 days/week; 8 hrs/day
Unit Energy Cost	\$0.06/KW-hr
Pumping Energy Efficiency	75%





## Full-Scale Design Criteria

Parameter	Value
Number of Contactors (operated in parallel)	4 (including one redundant contactor)
Contactor Diameter	8 ft
Resin Depth	5 ft
Resin Volume/Contactor	251 ft <sup>3</sup>
Total Volume of Resin Required	1,005 ft <sup>3</sup>
Regeneration Volume	3.5 BVs
Total Residual Waste Volume	13.5 BVs
Percent of Water Wasted (spent brine and rinse water)	1.9%
Maximum Feed-Water Capacity	2,548 gpm
Annual Salt Usage Rate	3,704 tons
Maximum Headloss Rate	2.9 psi/ft
Average Headloss Rate	1.9 psi/ft
Maximum Headloss	14 psi
Average Headloss	10 psi
Average Service Loading Rate	2.3 gpm/ft <sup>3</sup>
Regeneration Frequency (i.e., time between regenerations)	9 hours
Daily Average Waste Stream Flow Rate	43 gpm



## Budgetary Cost Estimate of a Full-Scale Ion-Exchange Treatment Plant for Perchlorate Removal in the San Gabriel Basin

<b>Parameter</b>	<b>Cost</b>
IX Equipment	\$640,000
Construction & Other Capital Costs	\$480,000
Resin Cost	\$125,000
Brine Line One-Time Connection Fee	\$264,000
Engineering, Legal, & Administrative Cost (@15%)	\$226,000
<b>Total Capital Cost</b>	<b>\$1,735,000</b>
Resin Replacement Cost	\$23,000/yr
Salt Cost	\$123,000/yr
Brine Disposal Cost	\$15,000/yr
Energy Cost	\$6,500/yr
Maintenance Cost	\$75,000/yr
Labor Cost	\$62,500/yr
<b>Total O&amp;M Cost</b>	<b>\$305,000/yr</b>
Amortized Capital Cost	\$139,000/yr
Total Annual Cost	\$445,000/yr
Annualized Water Cost	\$122/AF

